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COATINGS. ENAMELS

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OPACIFIED AND OPALINE ENAMELS ON PRECIOUS METALS

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The problems of enamel frits are examined. Enamel compositions are worked out using different opacifiers. It is shown how an opacifier affects the properties of and coverage by enamel. The reasons for opacification of a material are determined.

Key words: enamel, enameling, compositions, frits, enameling technology, opacification, opalescence.

Jewelry made from precious metals decorated with enamel is in demand again. Enameling in Rus' has been known since the 13 – 14th centuries. The most brilliant master enameller C. P. Fabergé, who became famous for his series of exquisite Easter eggs, is still considered to have worked at the juncture of the 19th and 20th centuries. The articles made by this great master are recognized standards in this field. And even though the world market places a strong emphasis on so-called cold enamels, hot enameling and painting on metal will always be in demand. Fabergé's palette contained up to 130 basic colors, including compositions with opacification and opalescence. This type of enamel with different degrees of opacification is in great demand by jewelers as a coating forming a background for painting on metal. In the USSR such enamels were made at the Druzhnaya Gorka Works (DGW) in Leningrad Oblast. Unfortunately, DGW was closed in 1990 and the prescriptions for the mixes were lost.

Attempts to obtain similar enamels have been made repeatedly in different countries. But it was found to be impossible to use the newly developed compositions under the conditions of an ordinary jeweler's workshop because of the presence of at least one of the indictors presented below:

– high deposition temperature for enamel on the substrate (above 800 °C); this results in deformation of the complicated piece of jewelry because of solder spreading;

– absence of a strong bond between the decorative enamel and substrate because of the large difference between their CLTEs (in experimental work copper fragments are used as the substrate; it is believed that if the enamel – copper bond is good, then the enamel is guaranteed to be suitable for deposition of precious metals also);

– low acid resistance of the enamel when the article is whitened in hydrochloric acid after kilning.

It should be noted that the enamels used by C. P. Fabergé and produced at the DGW did not have these drawbacks.

An enamel composition which has none of the drawbacks mentioned above was developed in the Department of the Chemical Technology of Glass and Sitals at the D. I. Mendeleev Russian Chemical Technology Institute. This is a potassium-lead-silicate glass, exhibiting good bonding to a copper substrate. The objective of the present study was to develop on its basis opalescent enamels with different degrees of opacification. It is known that the opacifiers used for obtaining opaline and frosted glasses are fluorine and phosphorus compounds [1 – 4]. Aside from fulfilling their principal function of opacifying glass, the additives introduced must not degrade either the coverage by the enamel or the physical–chemical properties of the enamel.

The mix for obtaining enamels consisted of pure and analytical grade raw materials. The powders were carefully mixed in a porcelain mortar to obtain a uniform mixture. The glasses for the enamels were made in corundum crucibles. To decrease losses of volatile components during glassmaking the crucibles with the mix were placed into a hot laboratory furnace heated to 1400°C and soaked in the furnace for 30 min. This amount of time was sufficient for heating the mix, melting, dissolving the components, and forming a uniform fined melt. The furnace itself is a laboratory setup with a 150 × 150 × 300 mm working space, heated with silicon

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carbide heaters. A platinum thermocouple was used to determine the temperature in the furnace.

The glasses were produced in the form of 30 – 50 mm in diameter disks (they were used to determine the physical–chemical properties) and frits (for deposition on a metal substrate). One-millimeter thick copper plates were used as substrates to deposit enamels in numerous experiments.

Fluorine was introduced into the glass in amounts to 2%[3] via potassium silicofluoride, but its presence in the composition did not produce any appreciable opalescence visible with the unaided eye. The adjustments made (heat-treatment of the material, performed to reveal its opalescence) at different temperatures to 700°C likewise did not decrease the light transmission of the glass. For this reason, fluorine was excluded from subsequent studies.

Another opacifier — phosphorus — was also introduced into the experimental material at the mix preparation stage. In terms of phosphorus oxide the content of this additive was 1.5, 2.0, 2.5, 3.0, and 3.5% (above 100%). Opalescence was observed in the glasses already after kilning, and their light transmission depended on the phosphorus oxide content. A low content of this component (1.5 and 2.0%) produced only barely perceptible opalescence even in glass samples with thickness approximately 5 mm. The effect was much stronger with additive contents 2.5, 3.0, and 3.5%; the opalescence of these glasses was quite noticeable and their light transmission was approximately 15 – 20%.

However, the effect achieved is clearly inadequate. The enamel layer on the metal is approximately 0.5 – 1.0 mm thick, and the opalescence of thin layers with such light transmission is practically unnoticeable with the unaided eye. The degree of opacification of the glass can be increased by making adjustments (heat-treating the glass). Ordinarily, the adjustment temperature is 600°C and the soaking time at this temperature is 4 h, while the entire temperature–time regime of heat-treatment lasts for approximately 8.5 h. At the same time it is obvious that an optimal concentration for the opacifier in the material and an adjustment regime exist for each glass composition individually [5, 6].

The effect of the heat-treatment time was studied for glass with phosphorus oxide content 2.5% and adjustment temperature 600°C. Two heat-treatment regimes were compared: long-time — 4 h soaking at the maximum temperature (total heat-treatment time 8.5 h) and short-time — 1 h soaking at the maximum temperature (total heat-treatment time 3 h). After adjustment the light transmission of the glasses in both cases was of the order of 1 – 2 %. In this connection, in all subsequent studies only the short heat-treatment regime was used.

The maximum soaking temperature during adjustment of the glasses in the experiments was 550, 600, 650, and 700°C. The investigations of their light transmission showed that the material with phosphorus oxide content 2.5% possesses the highest opacification. As the adjustment temperature increased the light transmission decreased from 20 to 0.5% (with glass thickness 5 mm). Thus, from the standpoint of light transmission glass with phosphorus content 2.5% makes it possible to obtain a wide spectrum of materials with different degrees of opacification. This is possible because the adjustment temperature is chosen to be in the range 550 – 700°C.

The glass is opacified because the uniform molten glass is divided into two or more phases separated by sharp boundaries and light is scattered at these interfaces. In this case, if the separation is effectuated by liquation, the material remains x-ray amorphous. If the glass is partially crystallized, x-ray phase analysis makes it possible to identify the form of the crystal phase which has precipitated. When studying the synthesized glasses presented in the present work, it was found that three different crystal phases are present in them. Lead orthophosphate $Pb_3(PO_4)_2$ is found in glasses at all phosphorus oxide concentrations. Potassium metaphosphate KPO_3 is present in glasses with phosphorus oxide content 2.0, 2.5, and 3.0%. Its maximum content coincides with the highest degree of opacification of the material. Potassium and barium double orthophosphate $KBaPO_4$ forms during heat treatment of glass with opacifier content 3.5%.

Investigations of the properties of opacified materials have shown that the introduction of phosphorus oxide in amounts to 3.5% did not change, for all practical purposes, either the physical – chemical properties of the glass or the capability of the enamel to form a smooth shiny glassy layer on the substrate surface at temperatures not exceeding 790°C. Thus, the opacified-glass compositions developed are fully suitable for enameling precious metals.

As a result, it has been established that phosphorus oxide can act as an opacifier in lead silicate enamels on precious metals; its optimal content is 2.5%. The degree of opacification of the material can be regulated by temperature heat-treatment (adjustment) of the glasses, during which partial crystallization of the glass occurs.

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[3] Here and below, content by weight.